

Soft x-ray emission spectroscopy of ions in solution

A. Augustsson¹, J.-H. Guo^{1,3}, D. Spandberg²,
K. Hermansson² and J. Nordgren¹

¹Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden

²Department of Materials Chemistry, Uppsala University, P.O. Box 538, S-75121, Uppsala, Sweden

³Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, USA

INTRODUCTION

Metal-ion transport in both aqueous- and polymer-solvent media involves continuous solvent-ligand exchange. Metal-ion coordination chemistry is therefore fundamental to these phenomena. The application of soft-x-ray absorption spectroscopy (SXAS) and soft-x-ray emission spectroscopy (SXES) to study wet samples has been hampered by the experimental difficulties of handling wet samples under high-vacuum conditions. Optical, infrared and Raman spectroscopies as well as magnetic resonance based methods are often used to determine the structure and the properties of these systems [1]. Here, we report the soft x-ray absorption and emission study of cations (Li^+ , Na^+ , K^+ , Mg^{2+} , and Al^{3+}) in water solution.

Experiment

The experiments were performed at beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator [2]. In the liquid phase measurements, the incident photon beam and secondary emission penetrated a thin silicon nitride window of 100 nm in thickness. XAS spectra of liquid water were recorded in x-ray fluorescence yield. XES spectra were recorded using a high resolution grating spectrometer [3].

Cation-solvent interaction

The solvated cation interaction can be monitored by examining the spectra of the solvent. The advantage of this approach is that the restriction to cations no longer applies. For example, it can be used in studying what happens when salts of the alkali and alkaline earth metals are added to aqueous solvent. Series of spectra at different salts at a given concentration exhibit an isosbestic point. In the figure experimental data

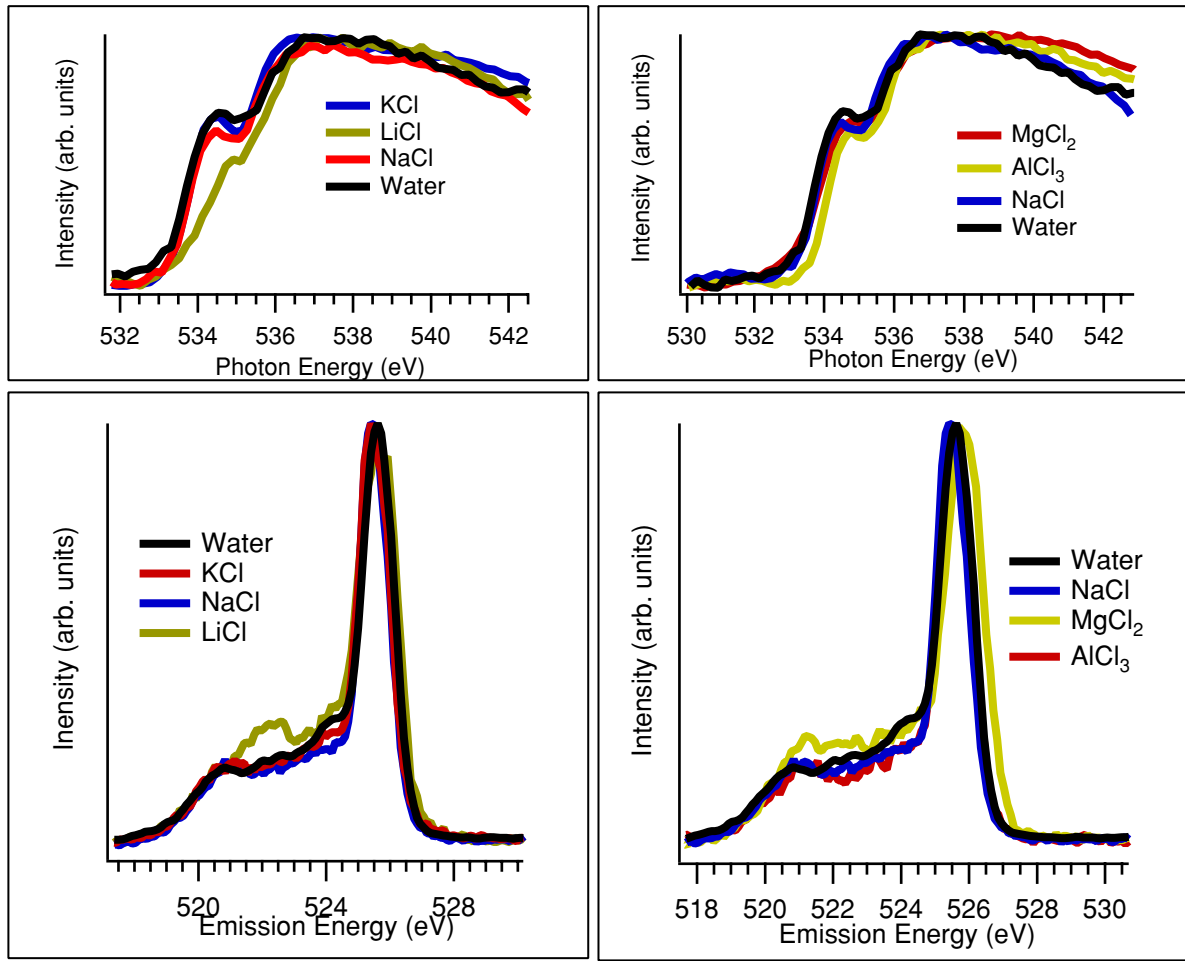


Figure 1: Top panels, O 1s XAS spectrum and bottom panels resonant O K-emission spectra of Ion solutions excited at the photon energy 534.5 eV

from ion-solutions are presented. Spectrum of pure water is also presented for comparison. The bottom panels shows the resonantly excited x-ray emission spectra, excited on the pre-edge in the absorption spectra at ~ 534.5 eV (top panels). The left panel shows a comparison of O 1s spectra of solutions with ions of varying sizes and the right panel shows spectra varying charge. In the emission spectra one observe that spectrum of Na^+ and Al^{3+} solutions are similar while the emission spectrum of the Mg^{2+} solution show a broadened main peak, and some distinct differences at lower energies. Comparing Na^+ and K^+ solutions a small difference is observed, while the smaller Li ion shows a large spectral effect both in absorption and emission. We are presently working with theoretical interpretation, to achieve a full understanding of the data.

References

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Principal investigator: E. Joseph Nordgren, Department of physics, Uppsala University,
Email: joseph@fysik.uu.se. Telephone: +46 18 4713554.